I. C. 7441 FEBRUARY 1948

UNITED STATES
DEPARTMENT OF THE INTERIOR
J. A. KRUG, SECRETARY

BUREAU OF MINES
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INFORMATION CIRCULAR

LABORATORY EQUIPMENT FOR THE ANALYSIS OF MINE ATMOSPHERES

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L. B. BERGER AND H. H. SCHRENK

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

LABORATORY EQUIPMENT FOR THE ANALYSIS OF MINE ATMOSPHERES[1]

By L. B. Berger[2] and H. H. Schrenk[3]

INTRODUCTION

The Bureau of Mines frequently receives requests for information and advice regarding the equipment necessary for establishing laboratories for the analysis of mine atmospheres. Such requests are made by mining companies, State mining departments, and other agencies concerned with the safety of mining operations. In many instances it is desired to install a complete laboratory, which will necessitate purchase of suitable gas-analysis apparatus and all the minor but important accessory equipment needed to carry on this type of work. Although publications that describe methods and techniques applicable to the analysis of mine atmospheres are available, it is not within the scope of such publications to give detailed information on laboratory equipment or design. Persons unfamiliar with laboratory practices and gas-analysis procedures may find it difficult to decide upon the proper equipment for their particular needs and to itemize the various accessories that must be obtained to set up a complete laboratory.

The purpose of this circular is to discuss the different types of equipment that may be used in the analysis of mine atmospheres, with particular regard to the application and limitations of each type. Information on the various accessory equipment needed in a laboratory for the analysis of mine atmospheres is given also, and suggestions on laboratory design are included. As much of the necessary equipment may be obtained from laboratory supply houses, the information should aid in arriving at estimates of the cost of proposed laboratories.

The procedures involved in the analysis of mine atmospheres are not described; such information is contained in publications referred to in this circular.

TYPES OF ANALYSES THAT MAY BE REQUIRED IN DETERMINING THE COMPOSITION OF MINE ATMOSPHERES

The analysis of mine atmospheres may be divided into two general classes with respect to the locations at which the atmospheres exist, namely, in ventilated and unventilated places.

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Analysis of the Air of Ventilated Places

In coal mines and in some other underground operations the percentage or concentration of methane in the air of ventilated places is of chief concern because of the potential hazard of explosion. The oxygen and carbon dioxide contents of the air are important mainly in that significant reductions in oxygen or increases in carbon dioxide may affect the health and efficiency of persons at work in such atmospheres.

The air of ventilated working places also may be contaminated by noxious or poisonous gases that are produced or liberated in the course of mining operations. Carbon monoxide may be introduced into the air through the use of explosives or of internal combustion engines and may be present in the air because of leakage of gases from sealed fire areas. The toxic oxides of nitrogen may be produced by the use of explosives and are present in the exhaust gases of internal combustion engines.

The following data are cited in regard to the concentrations or percentages of these different gases that must receive consideration in the analysis of mine atmospheres:

A publication of the Bureau of Mines (1)[4/] contains the following statement regarding the composition of the air of working places in bituminous-coal and lignite mines: "Air in which men work or travel shall be improved when it contains less that 19.5 percent oxygen, more than 0.5 percent carbon dioxide, or is contaminated with noxious or poisonous gases."

This publication also states, in substance, that only equipment and methods permissible for use in gassy mines shall be used in any mine in which 0.25 percent or more of methane is found in any open workings.

In regard to the toxic gases, it is generally considered[5/] that 0.01 percent by volume of carbon monoxide is the maximum concentration permissible in the air of working places in which exposure does not exceed 8 hours daily. The similar maximum for oxides of nitrogen is 0.0025 percent (25 parts per million, by volume).

From the foregoing it is evident that the quality of the air of working places must be maintained within close tolerances to meet these requirements and that the methods used in analyzing the air must be quite accurate and sensitive if analytical results of any value are to be obtained. For example, if the return air of a mine actually contains 0.20 percent of methane, it would be meaningless and a waste of time to analyze this air by a method whose accuracy is no better than 0.2 to 0.3 percent, because the results might be in error by an amount equal to or greater than the actual percentage of methane present. If the methane content of the air, as determined by

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4/ Figures in parentheses indicate items in the bibliography appended to this circular.

5/ The values cited in this paragraph are contained in many ventilation codes and are designated as the permissible maxima by the American Standards Association.

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analysis, is to be used in conjunction with a measured air-quantity value to calculate volume of methane liberated by the mine in a given time, the calculated result will be of little or no value unless an analytical method of maximum accuracy is used in determining the methane.

Likewise, if carbon monoxide is to be determined in the air of working places, from the standpoint of possible effects upon persons at work in these places, the analytical method must be sensitive to at least 0.01 percent of carbon monoxide.

Methods suitable for the analysis of the air of ventilated mine workings are described in a following section.

Analysis of Atmospheres of Unventilated Places

The term "unventilated places" refers to (a) face areas or dead ends through which the ventilating air is not coursed, (b) open, unventilated, abandoned sections, and (c) the areas behind fire seals or gas seals. The atmosphere in such places may contain considerable percentages of carbon dioxide and abnormal accumulations of nitrogen, and may be depleted of oxygen. The methane content may be below, within, or above the explosive range, and, in the case of fire seals, carbon monoxide may be present in concentrations ranging from traces to several percent. Certain of the gases in these atmospheres may be present in percentages beyond the range of equipment suitable for the analysis of air from ventilated places, and when such is the situation analytical apparatus designed to accommodate these higher concentrations of gases must be used. Some decrease in accuracy of determination may result from the use of such apparatus, but a high degree of accuracy is not required in analyzing the atmospheres of many unventilated places. For example, if a sealed fire area in a coal mine actually contains 35 percent methane, an error of a few tenths of a percent or even as much as 1 percent would have no significance or importance in interpretation of analytical results.

One exception to the above statement is in the determination of carbon monoxide in sealed fire areas. When an active fire in a coal mine is first sealed, the carbon monoxide content of the atmosphere in the sealed area may be 1 or 2 percent or more, and extreme accuracy in determination is not necessary, as such concentrations of carbon monoxide may be interpreted only as indicating that the fire still is active. As the fire nears extinguishment and the area cools, the carbon monoxide content will decrease gradually and finally will reach zero if the area is allowed to remain sealed long enough. In such instances it is important to determine mere traces of carbon monoxide, and an analytical method sensitive to at least 0.01 percent of carbon monoxide should be used.

Methods and equipment suitable for the analysis of atmosphere from unventilated places are described in a following section.

The foregoing discussion is intended to show that no one type of equipment or method is applicable to the analysis of all types of mine atmospheres. Suitable analytical results will be obtained only when the equipment or method used is the proper one under the circumstances.

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EQUIPMENT OR METHODS USED IN THE ANALYSIS OF MINE ATMOSPHERES

The following paragraphs present summarized descriptions of equipment and methods that may be used for the analysis of mine atmospheres, indicating the field of application and the limitations of each. The selection of suitable equipment and methods for a proposed laboratory depends upon the nature and scope of the analytical work to be done.

Haldane-Type Gas-Analysis Apparatus (2)

1. The Haldane-type apparatus is suitable for accurate determination of carbon dioxide, oxygen, methane, and nitrogen in the air of ventilated places.

2. Accuracy of determination is 0.02 to 0.03 percent.

3. Carbon monoxide and hydrogen may be determined, somewhat less accurately, in a limited range of concentration.

4. The apparatus is suitable for determination of high concentrations of carbon dioxide, abnormal accumulations of nitrogen, and depletion of oxygen.

5. The apparatus is not suitable for determination of methane in concentrations within or above the explosive range.

6. Laboratories established primarily for the purpose of maintaining adequate ventilation in working places should be equipped with Haldane-type apparatus.

7. A capable operator can analyze an average of 10 samples in duplicate per day: that is, two determinations of the carbon dioxide, oxygen, and methane contents of 10 samples.

Portable Orsat Gas-Analysis Apparatus (3)

1. The portable Orsat apparatus is suitable for determination of carbon dioxide, oxygen, carbon monoxide, methane, and nitrogen in the atmospheres of sealed areas or the analysis of oxygen-deficient atmospheres or considerable accumulations of carbon dioxide, methane, or nitrogen in unventilated places.

2. Accuracy of determination of carbon dioxide, oxygen, and carbon monoxide is 0.2 to 0.3 percent.

3. Methane may be determined in concentrations below, within, or above the explosive range with an accuracy of 0.2 to 1.0 percent, depending on the concentration of methane.

4. The apparatus is suitable for either laboratory or field use.

5. The apparatus is not suitable for the accurate determination of low concentrations (less than 2.0 percent) of methane in the air of ventilated

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places such as main returns, splits, etc., and is not suitable for the determination of carbon monoxide in concentrations less than 0.3 percent.

Laboratory Orsat Gas Analysis Apparatus (4) (5)

1. The laboratory-type Orsat apparatus has the same field of application as the portable Orsat, and, in addition, hydrogen and higher hydrocarbons such as ethane may be determined.

2. The apparatus is somewhat more accurate than the portable Orsat, but the accuracy is not adequate for the determination of low concentrations of methane in the air of ventilated places.

"Pyrotannic Acid" Method for Determination of Carbon Monoxide (6) (7) (8)

1. The pyrotannic acid method is suitable for the determination of low concentrations (0.01 to 0.20 percent) of carbon monoxide in the air of ventilated places or in the gases from sealed fire areas when the fire is nearing extinguishment and the area is cooling.

2. The method is suitable, also, for determination of carbon monoxide in the blood of persons overcome or killed by that gas.

3. The method is suitable for use in the field as well as in the laboratory.

4. The method is particularly suitable for occasional use or in laboratories where only a small number of samples are to be analyzed for carbon monoxide.

"Phosphomolybdic Acid" Method for Determination of Carbon Monoxide (9)

1. The phosphomolybdic acid method is suitable for the determination of low concentrations (0.002 to 0.06 percent) of carbon monoxide in the air of ventilated places or in the gases from sealed fire areas when the fire is nearing extinguishment and the area is cooling.

2. The method is more sensitive and accurate than the pyrotannic acid method for carbon monoxide but is more complicated in regard to apparatus and technique.

3. The method is best adapted to use in laboratories where a considerable number of samples are to be analyzed for carbon monoxide and where the method is in more or less continuous use.

4. The method is not suitable for field use.

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Phenoldisulfonic Acid Method for Determination of Oxides of Nitrogen (10)

1. The phenoldisulfonic acid method is suitable for determination of the toxic oxides of nitrogen in concentrations that may be encountered (a) in the air of working places after blasting, or (b) as a result of the use of internal combustion (Diesel) engines, or (c) in comparatively high concentrations such as may be present in the undiluted exhaust gases of internal combustion engines.

2. The method necessitates collection of samples in specially prepared containers.

3. The analytical procedure may be conducted only in a laboratory.

The foregoing summary of the application and limitations of different apparatus and methods used in the analysis of mine atmospheres is further condensed in table 1.

EQUIPMENT FOR SAMPLING MINE ATMOSPHERES

The selection of proper equipment for sampling mine atmospheres is of equal importance with the choice of analytical methods, because no matter what degree of care and skill may be exercised in the analysis, the results can be no better than the sample. A sample that has been improperly collected or one whose composition has changed because of faults in the sample container is worthless, and the results obtained by analysis of such a sample may be seriously misleading. The subject of sampling mine atmospheres is discussed in detail in Bureau of Mines Miners' Circular 34 (3); the following information applies to the various types of containers that may be used in collecting samples of mine atmosphere:

A vacuum-type container (fig. 1) is used almost exclusively by the Bureau of Mines for the collection of samples of mine atmosphere, because it has been found most suitable from the standpoints of freedom from leakage, ease of transportation underground, and durability in shipment. For details on the use of the vacuum-type container, see reference (3). After the sample has been withdrawn from this type of container and the analysis has been completed, the opened container is sent to a glass blower for repair, re-evacuation, and resealing. Use of this type container is practicable only where the necessary facilities for glass blowing and re-evacuation can be arranged for, as the cost of a new container for each sample collected would be unreasonably high.

Other types of glass sample containers are shown in figure 2, one type being closed by rubber-tubing connections clamped shut by screw clamps, and the other type being fitted with glass stopcocks. Such containers are rather vulnerable to breakage, and the type fitted with rubber-tubing closures should be used only when the samples will be analyzed shortly after collection, as some diffusion and loss of gases through the rubber may take place if several days elapse between sampling and analysis.

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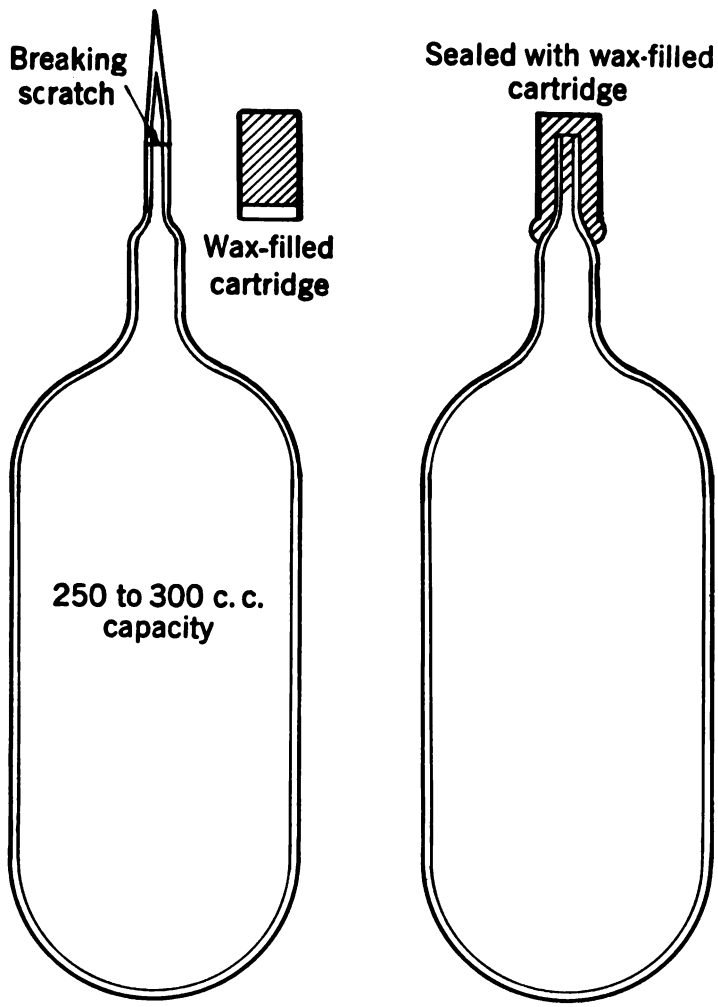

Figure 1. - Vacuum type sample container.

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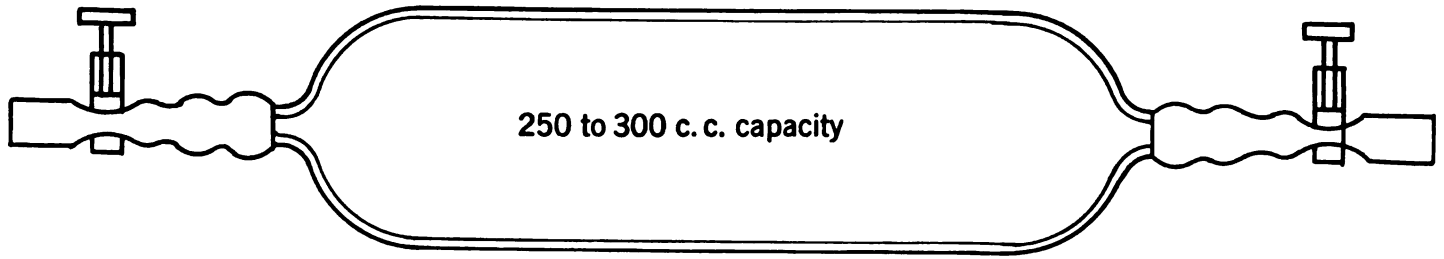
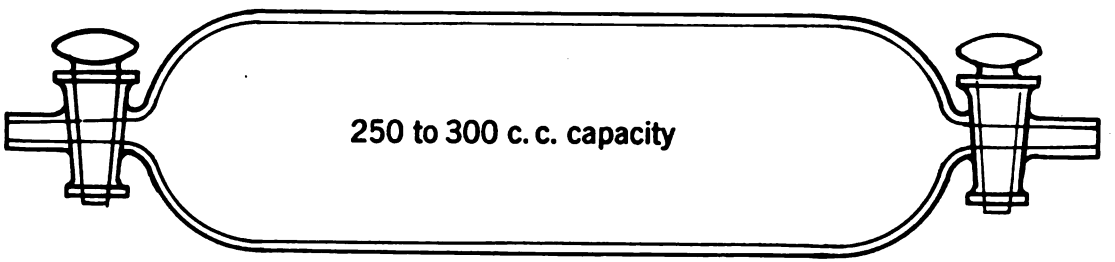


Type A



Type B

Figure 2. - Gas or liquid displacement type of sample container.

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TABLE 1. - Application and limitations of apparatus and methods for the analysis of mine atmospheres

Apparatus or method	Application and limitations
Haldane apparatus	Accurate determination of carbon dioxide, oxygen, and methane. Required for the accurate determination of low concentrations of methane in the air of ventilated places. Not suitable for determination of methane in percentages within, or above, the explosive range.
Portable Orsat apparatus	Analysis of atmospheres of sealed areas, oxygen-deficient atmospheres, and accumulations of methane, carbon dioxide, and nitrogen in unventilated places. Not suitable for accurate determination of low concentrations of methane in the air of ventilated places. Not suitable for determination of carbon monoxide in concentrations less than 0.3 percent.
Laboratory Orsat apparatus	Same field of application as portable Orsat, producing results of somewhat greater accuracy. In addition, hydrogen and higher hydrocarbons such as ethane may be determined. Not suitable for accurate determination of low concentrations of methane in the air of ventilated places.
Pyrotannic acid method for carbon monoxide	Determination of carbon monoxide in concentrations ranging from 0.01 to 0.20 percent. Determination of carbon monoxide in blood of persons overcome or killed by that gas. Suitable for laboratory or field use.
Phosphomolybdic acid method for carbon monoxide	Accurate determination of carbon monoxide in concentrations ranging from 0.002 to 0.06 percent. More sensitive and accurate than pyrotannic method, but more complicated in operation. Suitable for laboratory use only.
Phenoldisulfonic acid method for oxides of nitrogen	Determination of toxic oxides of nitrogen in concentrations of 5 p.p.m. or more. Specially prepared air-sample containers required. Suitable for laboratory use only.

Metal containers of the same general design as those shown in figure 2 may be used and are more durable than the glass containers. The metal stopcocks are more likely to leak than glass cocks, but if inspected and greased frequently will serve satisfactorily. The metal containers should be of

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brass, zinc, or other nonferrous metal. Iron containers are likely to remove oxygen from the sample through rusting of the interior of the container. Water must be used[6/] to displace sample from the metal-type container, and some loss of carbon dioxide from the sample through solubility is likely to result.

Some mining companies use rubber bags as containers for samples of mine atmosphere, inflating the bags and clamping off the inlets at the desired sampling locations. The bags are reported to be satisfactory for sampling atmospheres that are essentially normal air containing small percentages of methane or carbon dioxide. It seems possible, however, that if atmospheres containing high percentages of methane or carbon dioxide were sampled in this manner, some loss of these gases might occur unless the samples were analyzed soon after collection.

Bottles of the type used by druggists for magnesium citrate solution may be used as sample containers. This type of bottle is fitted with a glass stopper seating on a rubber gasket and held in place by a strong spring clamp. The rubber gaskets or washers must be in good condition to insure a gas-tight seal.

Specially prepared evacuated glass containers, as shown in figure 3, are used for collection of samples for determination of oxides of nitrogen. A small volume of liquid absorbent for oxides of nitrogen is placed in the container before it is evacuated and sealed. Preparation of these containers is described in detail in reference (10). A sample collected in this type of container may be analyzed only for oxides of nitrogen; if it is desired to determine other constituents of the atmosphere at the same location, an additional sample must be collected in one of the conventional containers.

The selection of sample containers depends on the type of analyses to be made, the extent of transportation of samples between mine and laboratory, the time that may elapse between sampling and analysis, and, in the case of the vacuum-type containers, the availability of facilities for evacuation and sealing of the containers.

RECORDING OF DATA

In a laboratory where samples of mine atmosphere are to be analyzed as a continuous operation, a systematic procedure should be adopted for identifying the samples and recording this information and the analytical results. A suggestion along this line is shown in figure 4, which is a reproduction of a label and number attached to mine-atmosphere sample containers used by the Bureau of Mines. The required information is inserted on the label by the collector of the sample at the time of sampling. The collector also fills in the required information on the card shown as figure 5, which is shipped to the laboratory along with the sample container to which it refers.

6/ If mercury is used as the displacing liquid, the soldered joints of metal sample containers will be destroyed by amalgamation.

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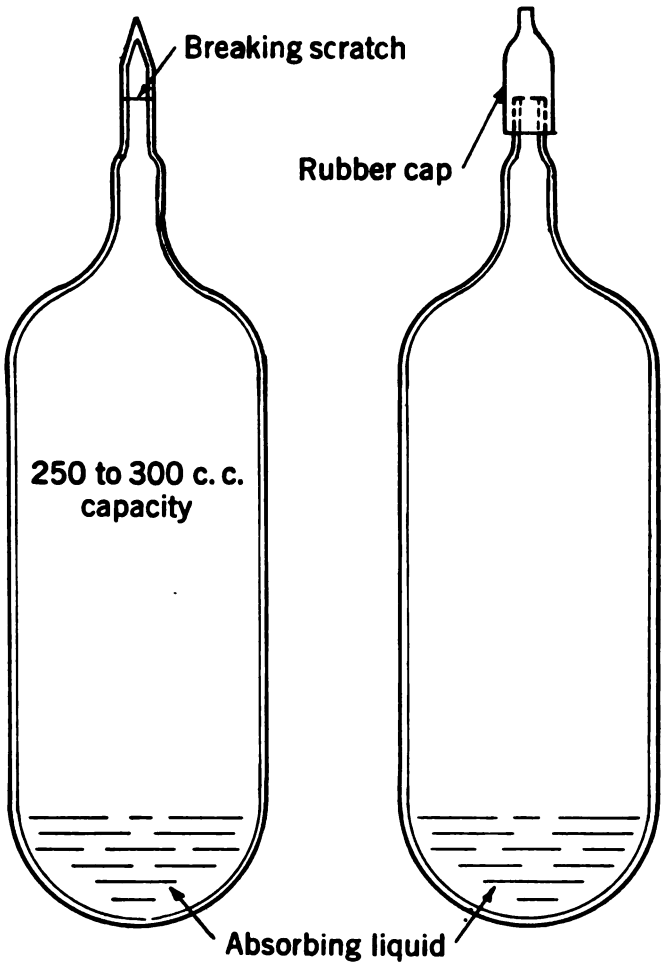

Figure 3. - Special evacuated container for sampling for oxides of nitrogen.

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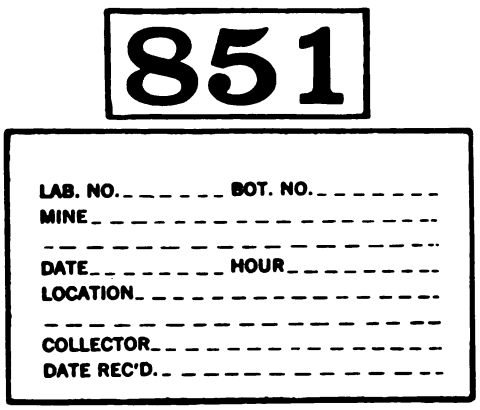
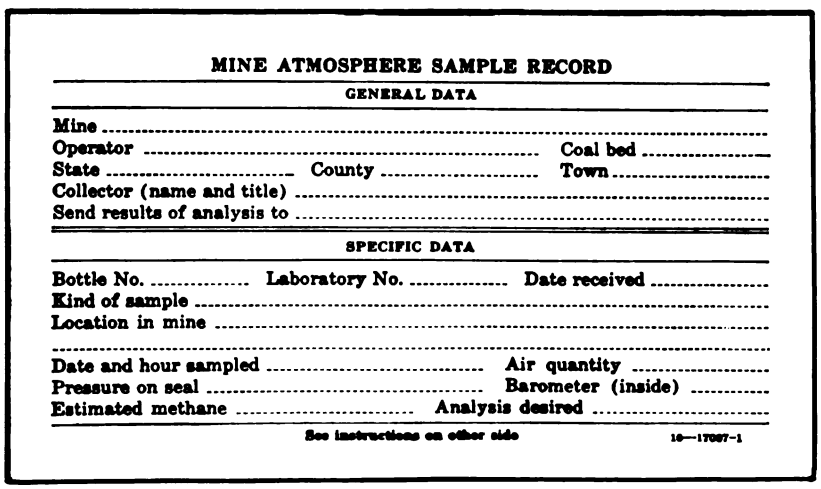


Figure 4. - Label and number on vacuum sample container.



MINE ATMOSPHERE SAMPLE RECORD

GENERAL DATA

Mine .....
Operator ..... Coal bed .....
State ..... County ..... Town .....
Collector (name and title) .....
Send results of analysis to .....

SPECIFIC DATA

Bottle No. ..... Laboratory No. ..... Date received .....
Kind of sample .....
Location in mine .....
.....
Date and hour sampled ..... Air quantity .....
Pressure on seal ..... Barometer (inside) .....
Estimated methane ..... Analysis desired .....

See instructions on other side 16—17087-1

Figure 5. - Mine atmosphere sample record which accompanies sample container.

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	Burette Reading	Corrected Reading	Difference	Per cent	Burette Reading	Corrected Reading	Difference	Per cent	Burette Reading	Corrected Reading	Difference	Per cent
Volume of sample taken												
Carbon dioxide												
Unsaturated hydrocarbons												
Oxygen												
Hydrogen by CuO at 300° C												
Carbon monoxide by CuO at 300° C												
Oxygen (or air) added												
Total volume												
Volume after burning												
Volume after CO_2 absorption												
Volume after second burning												
Volume after second CO_2 absorption												
Total contraction												
Total CO_2												
Residual O_2												
Total oxygen												
Methane												
Ethane												
Total paraffins												
Nitrogen												

Apparatus No. _____ *Date* _____ *Chemist* _____

Figure 6. - Form for recording data in the analysis of mine atmospheres.

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When the sample container and card are received at the laboratory, a serial number is stamped on the card and also on a form for recording the analytical data (fig. 6). This serial number thereafter identifies the sample and the results of its analysis. After the sample has been analyzed and the results have been reported, the data card and the analysis form are filed. It is preferable to keep all original analytical data on file in the laboratory. Any suitable form may be used in reporting the analytical results, so long as the sample is properly identified as to location, date of sampling, etc.

DETAILED LIST OF EQUIPMENT

The following section contains a detailed list of items necessary in connection with the various types of equipment or methods applicable to the analysis of mine atmospheres. The items are listed on the basis that complete laboratory facilities must be obtained. There is some duplication in the listing, in that some items that are needed for one type of apparatus or method may be suitable for use with another. Many of the items listed in connection with the Haldane apparatus are suitable for use in other gas-analysis procedures. The number or quantity of the items needed depends, of course, upon the size of the proposed laboratory. Most of the items may be purchased from laboratory supply houses. Some may be constructed by the prospective user if he so desires. The purposes of the various items listed are explained in the references cited in connection with each apparatus or method.

Haldane Apparatus (2)

Apparatus assembly. - The apparatus preferably should be obtained as a complete unit, including the supporting frame, all necessary glass parts, rubber tubing connections, and transformer and rheostat for power supply to combustion pipette. The transformer and rheostat are included in the assembly of some commercial apparatus. With others it may be necessary to purchase transformer and rheostat separately. The capacity of the transformer should be at least 150 watts, the primary should be suitable for use on the voltage and frequency available in the laboratory, and secondary voltage should be 6 to 8. The rheostat should be capable of carrying 2 to 3 amperes without overheating.

Spare parts for Haldane apparatus. - It is good policy to keep on hand a supply of spare glass and electrical parts for the apparatus, as breakage or failure of a single part may make the whole apparatus inoperative. Some No. 28, B. & S.-gage, platinum wire should be on hand for replacing burned-out or broken coils in the combustion pipette. Approximately 3 inches of wire is required for one coil.

Rubber tubing. - A supply of rubber tubing should be kept on hand, as connections on the apparatus must be replaced from time to time. For most commercial apparatus the following sizes are suitable:

For manifold - 3/16-inch inside diameter, 1/16- or 3/32-inch wall, pure gum.

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For lower connection to carbon dioxide pipette - 1/4-inch inside diameter, 3/32-inch wall, pure gum or sulfur-free rubber, or chemical-resistant synthetic.

For leveling bulbs - 3/16-inch inside diameter, 1/8-inch wall, nitrometer or other durable tubing.

It is not wise to overstock on rubber tubing, as it may deteriorate in time, even though not in use, unless stored in an inert atmosphere, such as nitrogen.

Chemicals. - The chemicals required in the actual analytical operations of the Haldane apparatus are potassium hydroxide and pyrogallic acid. Carbon dioxide is absorbed by a solution of potassium hydroxide, and oxygen by a mixture of solutions of potassium hydroxide and pyrogallic acid. Preparation of these solutions is described in references (2) and (3). The solutions may be purchased from some chemical supply houses or may be prepared by the user of the apparatus. The approximate quantities of the reagents, in the solid form, required for analysis of 1,000 mine-air samples are 10 pounds of potassium hydroxide (electrolytic grade) and 1/2 pound of pyrogallic acid.

Mercury is used as the confining liquid in the burette and combustion pipette of the Haldane apparatus. Approximately 5 pounds are required. For maximum accuracy (particularly in the determination of carbon dioxide, which is quite soluble in water), mercury should be used as the medium for displacing the air sample from its container into the analytical apparatus. Mercury may be employed for this purpose only when glass sample containers are used. Metal sample containers usually are fabricated with soldered joints, which are destroyed by amalgamation when brought into contact with mercury. A welded-steel mercury container suitable for use in connection with the displacement of air samples is shown in figure 7. A container of this type requires about 35 pounds of mercury. When considerable quantities of mercury are required, it may be advantageous to purchase it in flask (76-pound) lots.

Mercury used in the analysis of gases should be clean and, particularly, should not be contaminated with caustic materials that will introduce errors in the determination of carbon dioxide and methane by premature removal of carbon dioxide from the sample in the apparatus. If the mercury used in displacing the sample from its container is contaminated with caustic material, carbon dioxide will be removed from the sample before it is introduced into the apparatus. For this reason, equipment should be available for cleaning the mercury by acid treatment. The device shown in figure 8 is convenient for this purpose. The mercury first is strained through a cloth to remove grease and floating foreign matter, and then is placed in the reservoir at the top of the apparatus, from which it is allowed to flow slowly through a coarse cloth or other porous material, which breaks the stream of mercury into small particles or droplets. These particles of mercury descend through the cleaning mixture (5 parts by volume of nitric acid and 95 parts of water) in the long column. The acid-scrubbed mercury collects at the seal at the

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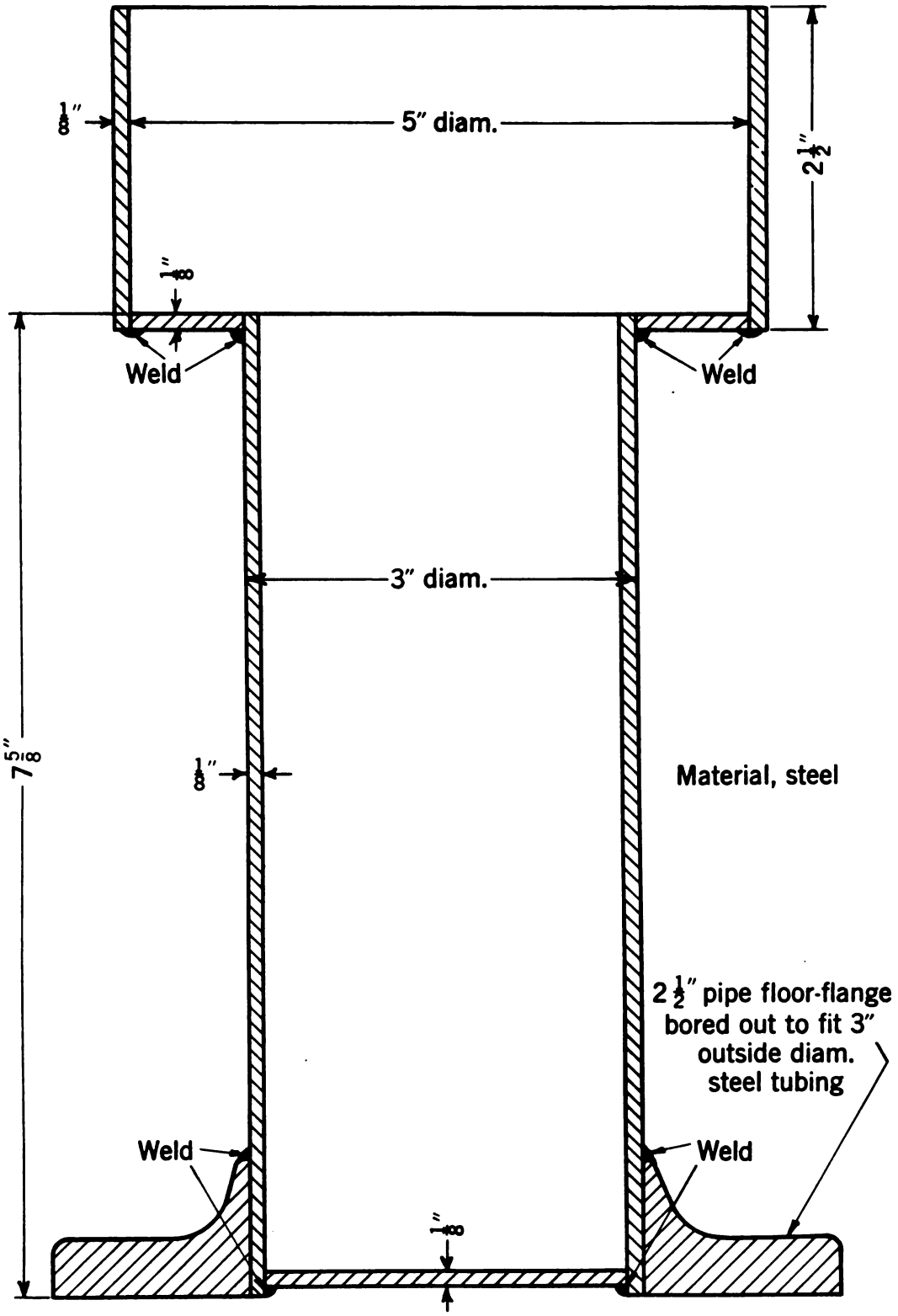

Figure 7. - Container for mercury used in displacing air samples.

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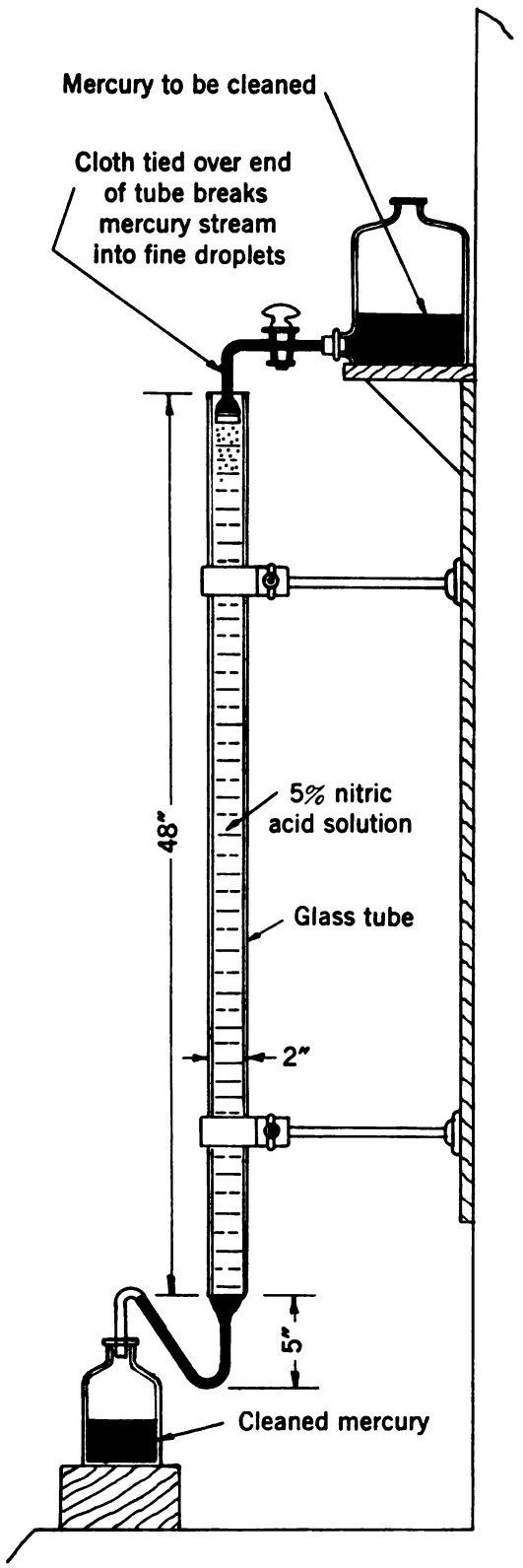

Figure 8. - Tower for acid-cleaning mercury used in gas analysis.

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bottom of the column and may be withdrawn as needed. Vacuum stills[7] may be used in laboratories where large quantities of mercury are to be cleaned.

A supply of distilled water should be available in the laboratory for the preparation of solutions and for rinsing glass parts of the apparatus after cleaning. For small laboratories, it may be simpler to purchase distilled water than to install a still.

Nitric and sulfuric acids should be available for cleaning purposes. A cleaning mixture of sulfuric and chromic acids is effective in removing grease films or deposits from the interior of the gas burette. One bottle each (approximately 2-1/2 liters) of nitric and sulfuric acids would be the minimum supply for a small laboratory. Organic solvents, such as gasoline or benzene, never should be used in cleaning any part of the gas-analysis apparatus.

If solutions are to be prepared in the laboratory, a set of scales and weights should be provided for weighing the chemicals. A platform-type scale, commonly called a "trip balance", sensitive to 1/10 gram, is suitable for this purpose.

Glassware. - A supply of glass beakers should be available for preparing and dispensing solutions, adding cleaning solution or water to the gas burette, and for similar purposes. Suggested sizes are 100 c.c., 500 c.c., and 4,000 c.c. As glassware of this type is rather fragile, it is advisable to have several of each size.

Glass graduates, or measuring cylinders, are necessary in preparing solutions. Suggested sizes are 100 c.c. and 1,000 c.c.

Glass funnels are convenient for adding solutions to the pipettes of the apparatus, for filling reagent bottles with solutions, etc.

Magnesium citrate bottles fitted with glass stoppers seating on rubber gaskets and held in place by spring clamps are convenient containers for storing the gas-analysis solutions. It is preferable to use several small containers rather than one large one for storing the oxygen-absorbing reagent, as in this way only a small volume of reagent comes into contact with air when the bottle is opened.

Soft glass tubing of both "shell" and "capillary" types is convenient for making connections to sample containers and for other purposes. Outside diameter of such tubing should be about 7 m.m.; inside diameter of the capillary tubing should not be less than 2 m.m. If the tubing is to be bent to shape in the laboratory, a Bunsen burner with a "wing" top will needed.

Compressed air. - In operating the Haldane apparatus, low-pressure (2 to 3 pounds per square inch gage) compressed-air is needed to cool the

7/ Kleiber, M., A Simple Apparatus for Mercury Distillation: Science, vol. 75, 1932, p. 196.

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combustion pipette and to stir the water in the jacket of the burette. If compressed air is not available at the laboratory, a small positive-pressure rotary blower driven by a fractional-horsepower motor will answer as an air supply. Such blowers may be obtained from laboratory supply houses.

Miscellaneous materials and tools. - A supply of suitable grease is necessary for lubrication of the stopcocks of the gas-analysis apparatus. As proper greasing of the stopcocks is an important part of preparing the apparatus for use, it is best to obtain a grease specially compounded for this purpose from a laboratory supply house. Ordinary pipe cleaners are useful for removing excess grease from stopcock bores, and soft cotton cloth is needed to wipe grease from the ground surfaces of stopcocks.

Triangular files, pliers, screw drivers, and soft copper wire (No. 22 B. & S. gage) will be found necessary in maintaining and adjusting the apparatus.

Portable Orsat Apparatus (3)

A number of types and designs of portable apparatus are available for the analysis of various gaseous mixtures. For the analysis of mine atmospheres, the apparatus should be fitted with a straight 100 c.c. burette (no bulb at top of burette) and should be suitable for the determination of carbon dioxide, oxygen, carbon monoxide, and methane. The first three gases are determined by absorption, and methane is determined either by combustion on a heated platinum-wire coil, or by oxidation on a heated, specially prepared catalyst. In the type of apparatus using the combustion pipette a shield of wire screen or shatter-proof glass should be provided to protect the operator in event of an explosion. If the apparatus is fitted with a transformer or other electrical equipment, the purchaser should specify voltage and frequency to conform with that available in the laboratory. The combustion pipette of some types of apparatus may be operated on dry cells (No. 6) when used in the field. Such batteries should not be obtained until the apparatus actually is to be used, as they deteriorate in storage.

Many of the items listed under the Haldane apparatus are suitable for use in connection with the portable Orsat apparatus. Such items include rubber tubing, glass tubing, stopcock grease, sulfuric acid, platinum wire for the combustion pipette, and solutions for the absorption of carbon dioxide and oxygen. Carbon monoxide usually is determined with the portable Orsat apparatus by absorption in cuprous chloride solution. See reference (3). One pound of cuprous chloride (solid), one bottle (6 pounds) of chemically pure hydrochloric acid, and 1/4 pound of stannous chloride (solid) will make enough of the cuprous chloride reagent to analyze 100 to 300 samples, depending on the percentage of carbon monoxide in the samples.

The confining liquid (water) in the burette and combustion pipette of the portable Orsat apparatus is maintained in a slightly acid condition by the addition of sulfuric acid. A small quantity of an "indicator" (methyl orange) is added to the water and colors it red so long as the water remains acid. One ounce, or even a smaller quantity, of methyl orange indicator will suffice for any ordinary needs.

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When the portable Orsat apparatus is used in the laboratory, many of the facilities provided for the Haldane apparatus may be used. These include power supply, compressed air for cooling the combustion pipette, vessels in which samples are displaced from their containers, etc.

When the portable Orsat apparatus is used in the field, as in analyzing gases from a sealed fire area in a coal mine, the analyst also may be responsible for collecting gas samples. In such situations the sampling equipment required, in addition to suitable sample containers, consists of 4 to 6 feet of soft copper tubing (1/4-inch outside diameter) for sampling through seals, a rubber aspirator bulb for pumping gas through the sampling tube, a water gage (a glass U-tube which may be made in the laboratory) for measuring gas pressure on seals, and suitable rubber tubing connections. Sampling techniques are discussed in detail in Bureau of Mines Miners' Circular 34 (3).

Laboratory-Type Orsat Apparatus (4) (5)

The laboratory-type Orsat apparatus suitable for the analysis of mine atmospheres usually is fitted with a straight 100 c.c. burette, three pipettes for the determination of carbon dioxide, oxygen, and carbon monoxide by absorption, and a combustion pipette for determination of methane and other combustible gases. To obtain maximum utility from this type of apparatus, it should include a tube containing copper oxide (which may be heated by an electric furnace) for the determination of carbon monoxide and hydrogen simultaneously or individually. With this arrangement, analysis may be made for four combustible gases (carbon monoxide, hydrogen, methane, and ethane). In some commercial apparatus the combustion (hot-wire) pipette is replaced by a tube of specially prepared catalyst for the combustion of methane and ethane. For maximum accuracy, mercury should be used as the confining liquid in burette and combustion pipette or tube. In the type of apparatus employing the combustion pipette, a shield of wire screen or shatterproof glass should be provided to protect the operator in event of an explosion. Electrical accessories should be specified, in regard to type of current, voltage, and frequency, to conform with the power supply available in the laboratory.

Many of the items mentioned in connection with the Haldane and portable Orsat types are suitable for use with the laboratory- type Orsat. These include rubber tubing, stopcock grease, cleaning solutions, sample-displacement vessels, compressed-air for cooling the combustion pipette and copper oxide tube, and reagents for the absorption of carbon dioxide and oxygen (2) (3). Cuprous chloride solution may be used for the absorption of carbon monoxide, as described in reference (3), although a preferred reagent for this purpose in the laboratory-type Orsat is composed of cuprous sulfate, beta-naphthol, and sulfuric acid, as described in references (3) and (7). This reagent may be purchased already prepared from some laboratory supply houses that specialize in gas-analysis equipment.

Pyrotannic Apparatus for Determining Carbon Monoxide (6) (7) (8)

The pyrotannic apparatus may be purchased as an essentially complete unit consisting of color standards, blood lancet, blood-dilution pipette,

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required test tubes, and a supply of the pyrotannic reagent. This reagent consists of equal parts, by weight, of pyrogallic and tannic acids thoroughly mixed and ground together to a fine powder. One ounce of each of the ingredients will make enough of the mixture to conduct more than 1,000 tests or analyses. The mixed reagent must be kept in a tightly-stoppered bottle, as it will absorb moisture from the air. In the analysis of air samples by the pyrotannic-acid method, any glass bottle that may be stoppered tightly will serve as a sample container. The volume of the sample bottles must be known, however, as volume of sample enters into the calculation of the percentage of carbon monoxide in the air sample. Bottles of 100 to 250 c.c. capacity are suitable.

Phosphomolybdic Acid Method for Determining Carbon Monoxide (9)

A list of equipment for determination of carbon monoxide by the phosphomolybdic acid method is not included in this publication, as the reference cited contains this information in detail.

Phenoldisulfonic Acid Method for Determining Oxides of Nitrogen (10)

Reagents. - The following reagents are required in the determination of oxides of nitrogen in mine air samples:

Potassium hydroxide.

Phenoldisulfonic acid reagent, which is prepared from concentrated sulfuric acid, fuming sulfuric acid, and phenol.

Litmus or other indicating test paper.

Ammonium hydroxide.

Potassium nitrate.

Distilled water.

Specially prepared glass containers are necessary in the collection of samples for determination of oxides of nitrogen. It is possible that these containers, already prepared, may be obtained from laboratory supply houses that specialize in gas-analysis equipment. If the containers are to be prepared in the laboratory, the following reagents will be required:

Tenth-normal sulfuric acid solution, reagent grade.

Hydrogen peroxide, 30 percent, reagent grade.

The specially prepared sample containers described in reference (10) are intended primarily to furnish a simple and convenient method for sampling underground atmospheres for the determination of oxides of nitrogen. The preparation of such containers requires glass-blowing facilities and a pump for evacuating the container before it is sealed. Other means suitable

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or collection of the samples might be devised if these facilities are not available.

A small rubber cap is used to seal the vacuum-type container for oxides of nitrogen after the sample has been collected. These caps are known as "rubber policemen" in laboratory parlance and may be obtained from laboratory supply houses.

Apparatus. - In the analytical procedure, the following equipment is required:

Glass beakers of 150 c.c. capacity, into which the liquid absorbent from the sample container is transferred.

Cover glasses to fit the above beakers. These are to prevent loss of material from the beakers when their contents are evaporated.

An electric hotplate is used for the evaporation procedure.

Graduates and pipettes suitable for the measurement of reagent volumes are required, as indicated in reference (10).

The final step in determination of oxides of nitrogen is a comparison of the intensity of color produced by chemical treatment of the samples, with the color of "standards" similarly processed. The comparison may be made visually by matching the colors in Nessler tubes, to which the colored solutions are transferred. This method is the simplest and least expensive for the small laboratory, where only a limited number of samples are to be analyzed for oxides of nitrogen. When a greater number of analyses are to be made, or maximum accuracy is desired, a colorimeter of the photoelectric type is preferable. A colorimeter of this type may be used to advantage also in the determination of carbon monoxide by the "phosphomolybdic acid" method (9).

LABORATORY PLAN

The required size or floor space of the proposed gas-analysis laboratory will depend, of course, on the volume and variety of analytical work to be done. In general, the equipment is best housed in a separate room used only for gas analysis. The room should be arranged so that it is free of cross drafts and not subject to sudden changes of temperature. Facilities such as electric power, tap water, compressed air, and fuel gas should be available.

In addition to a suitable bench for mounting the gas-analysis apparatus, the laboratory equipment should include a flat-top table or bench that may be used in the preparation of solutions or for analytical work, a sink, shelves for storing chemicals and gas-sample containers, and lockers in which spare glass parts of the gas-analysis apparatus may be stored. Means should be provided for the orderly filing of sample records and analytical results.

The method of mounting the gas-analysis apparatus will depend on the structural features of the particular equipment obtained. The Haldane-type

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apparatus or the laboratory Orsat should be more or less permanently installed on a stout table or bench that will not be subject to shock or vibration from any source. The apparatus should be located so that it is not subject to sudden changes in temperature, as by drafts from open doors or windows or by excessive heat from room-heating appliances.

Figure 9 shows the design of a bench for gas-analysis apparatus used in the Gas Analysis Laboratory of the Bureau of Mines. The figure shows a section of bench suitable in size for mounting one apparatus; the length of bench may be increased to accommodate any desired number of units, and for a large laboratory, apparatus may be mounted on both sides of the bench.

The figure as drawn represents the mounting of a Haldane-type apparatus, but the laboratory-type Orsat may be installed similarly. The manifold, pipettes, and electrical controls are attached to panel a; the burette is supported by clamps attached to rod b; the leveling bulb is supported on rod c. Rods b and c are clamped to the pipe framework d, which extends the length of the bench and permits lateral adjustment of the rods to any desired position. It may be noted that panel a is supported on a short length of pipe, d', attached to the center partition g, as are frames d and a shelf for the sample-displacement vessel m. With this system of mounting, the bench top f is left clear of apparatus supports, and spilled mercury may be removed by brushing it from the bench top, which slopes slightly to the rear, into the slot e, from which it drops into welded-steel trough k and thence into reservoir l, from which it may be recovered.

As there is some potential health hazard from the inhalation of mercury vapor in a laboratory where this material is used, provision should be made for ventilation of the gas-analysis laboratory. The most prolific sources of mercury vapor are the fine droplets of mercury that are formed when it is spilled to the bench top. Accordingly, ventilation is most effective if provided at that level rather than by an overhead hood or by general ventilation of the room. As shown in figure 9, the center partition g is hollow, being formed of 2-inch plank bolted to channel-iron frames, h. The enclosed space, i, communicates through duct j with an exhaust fan, so that a continuous stream of air is drawn over the bench top and into i through slot e, as shown by the heavy arrows in the figure. In the Gas Analysis Laboratory of the Bureau of Mines, approximately 250 cubic feet per minute of ventilating air is provided in this manner for each gas-analysis apparatus, and tests of the laboratory air have shown it to be essentially free of mercury vapor.

As shown in figure 9, approximately 3-1/2 feet of bench is required for an apparatus, and a clear floor space of at least 3-1/2 by 3-1/2 feet should be provided in front of the bench for the operator.

APPROXIMATE COST OF MINIMUM LABORATORY FACILITIES

On the basis of prices current at the time of preparing this paper, it is estimated that the cost of establishing minimum laboratory facilities for the analysis of mine-air samples would be in the neighborhood of $1,000. The equipment would include one Haldane-type gas-analysis apparatus, spare

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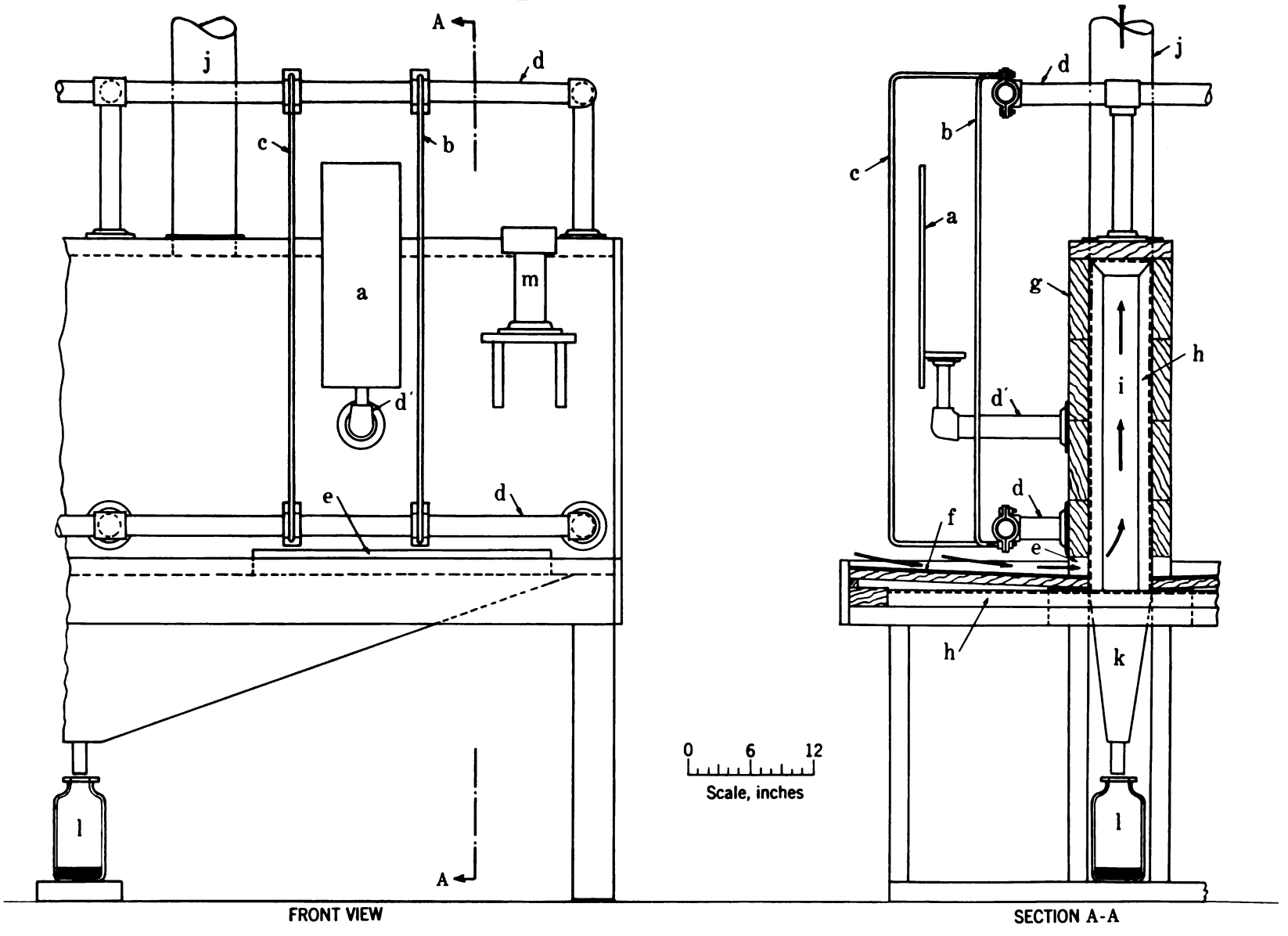

Figure 9. - Bench for gas analysis apparatus, as used in Bureau of Mines gas analysis laboratory.

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parts, reagents and mercury, a reasonable number of sample containers, and the accessory equipment necessary in the conduct of the work. Where laboratory facilities are available, this initial cost might be reduced substantially. The cost of additional gas-analysis units, such as a portable Orsat apparatus, would be confined essentially to the price of such units, as the cost of most of the required accessory equipment would be covered by the initial expenditure for these facilities.

SUMMARY

The purpose of this paper is to supply information on the equipment needed to install laboratories for the analysis of mine atmospheres. The various types of apparatus and methods that may be used for this purpose are discussed, pointing out the field of application and the limitations of each. It is emphasized that no one type of apparatus or method is applicable to the analysis of all types of mine atmospheres. Information is supplied, also, on the various accessory equipment needed, and suggestions as to certain features of laboratory design are included.

References are given to publications that describe in detail the procedures involved in the analysis of mine atmospheres.

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